IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Applicant	: Larry W. Hrubesh	Attorney Docket	: IL-10413
Serial No.	: 10/050,437	Art Unit	: 1754
Filed	: January 15, 2002	Examiner	: P. Lish
For	: Lightweight, High Strength Carbon Aerogel Composites and Method of Fabrication		

RESPONSE TO NOTIFICATION OF NON-COMPLIANT APPEAL BRIEF

In response to the Notification of Non-Compliant Appeal Brief mailed August 18, 2006, please enter the attached Corrected Appeal Brief.

All required fees have previously been paid, except the one month extension, for which a petition is attached. The Commissioner is hereby authorized to charge any fees which may be required or credit any overpayment to Deposit Account **501913**.

Respectfully submitted,

John P. Wooldridge

John P. Wooldridge
Attorney for Appellants
Registration No. 38,725
Tel. No. 808-875-0012

Dated: October 18, 2006

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Applicant	: Larry W. Hrubesh	Attorney Docket	:	IL-10413
Serial No.	: 10/050,437	Art Unit	:	1754
Filed	: January 15, 2002	Examiner	:	P. Lish
For	: Lightweight, High Strength Carbon Aerogel Composites and Method of Fabrication			

CORRECTED BRIEF ON APPEAL

This is an appeal to the Board of Patent Appeals and Interferences from the final rejection of Claims 1, 4, 8 and 18 mailed April 19, 2005. On August 19, 2005, a timely Notice of Appeal was filed.

I. REAL PARTIES IN INTEREST

The real parties in interest are the Regents of the University of California and the United States of America as represented by the United States Department of Energy.

II. RELATED APPEALS AND INTERFERENCES

Appellant knows of no other appeals or interferences that will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

III. STATUS OF CLAIMS

Claims 1, 4, 8 and 18 are pending on appeal and stand rejected. The rejection of claims 1, 4, 8 and 18 is appealed. Claims 2, 3, 5-7, 9-17 and 19 were previously canceled. A copy of the claims on appeal is set forth in the Claims Appendix.

IV. STATUS OF AMENDMENTS

All amendments have been entered.

V. SUMMARY OF CLAIMED SUBJECT MATTER

Independent claim 1 is a method for producing carbon aerogel composites comprising the steps of (i) infiltrating a solution containing a plurality of carbon aerogel precursors into a pre-formed polymer foam, or fiber-mat (paragraph 13, lines 5-6), (ii) allowing said solution to gel such that it encapsulates at least part of the pre-formed polymer foam or fiber-mat to form a gelled composite (paragraph 13, lines 6-7), (iii) drying the gelled composite to form a dried composite such that the surface tensile forces are reduced (paragraph 13, lines 7-9), and (iv) pyrolyzing the dried composite wherein the preformed polymer foam or fiber-mat and the carbon aerogel decompose simultaneously such that they remain essentially in contact at their interfaces to form a monolithic glassy carbon material (paragraph 13, lines 9-13).

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPPEAL

Whether claims 1 and 18 are anticipated by Droege.

Whether claims 4 and 8 are unpatentable over Droege.

Whether claims 1, 4, 8 and 18 are unpatentable over Pekala et al in view of Kaschmitter et al.

VII. ARGUMENT

Are claims 1 and 18 anticipated by Droege?

As indicated in the Declaration under 37 CFR §1.132 filed January 20, 2005, claim 1 of the present patent application includes a drying step that reduces surface tensile forces so that the organic aerogel and the preformed polymer foam/fiber-mat that it encapsulates, are essentially monolithic. After pyrolysis, they remain essentially in contact at their interfaces to form a monolithic glassy carbon material. Claim 1 recites: "drying the gelled composite to form a dried composite such that the surface tensile forces are reduced." As discussed in the Declaration, the Droege reference teaches a drying method that does not reduce surface tensile forces adequately to produce a monolithic composite, nor to form an essentially monolithic composite when pyrolized. The reference does not teach how to produce an essentially monolithic foam/mat aerogel composite. Claim 18 should be allowable at least because it depends from claim 1. Therefore the rejection should be withdrawn.

Are claims 4 and 8 unpatentable over Droege?

Claims 4 and 8 should be allowable at least because they depends from claim 1, which should be allowable over Droege as discussed above. Therefore the rejection should be withdrawn.

Are claims 1, 4, 8 and 18 unpatentable over Pekala et al in view of Kaschmitter et al?

As indicated in the Declaration under 37 CFR §1.132 filed January 20, 2005, in both Pekala and Kaschmitter, the pore size is required to be large enough so that fluid

(electrolyte) can flow. Thus, neither reference teaches a method for producing a monolithic foam/mat aerogel composite. The composites produced by the Pekala and Kashmitter patents do not exhibit the same bulk properties as a monolithic aerogel because the average pore size is relatively large. In fact, such large pores, which enable easy fluid transport through the material, are essential for the application of energy storage. Therefore the rejection should be withdrawn.

Accordingly it is submitted that the rejections of claims 1, 4, 8 and 18 are improper and should be reversed.

Respectfully submitted,

John P. Wooldridge
Attorney for Appellants
Registration No. 38,725
Dated: October 18, 2006   Tel. No. (808) 875-0012

VIII. CLAIMS APPENDIX

1. A method comprising:

infiltrating a solution containing a plurality of carbon aerogel precursors into a pre-formed polymer foam, or fiber-mat,

allowing said solution to gel such that it encapsulates at least part of the pre-formed polymer foam or fiber-mat to form a gelled composite,

drying the gelled composite to form a dried composite such that the surface tensile forces are reduced, and

pyrolyzing the dried composite wherein the preformed polymer foam or fiber-mat and the carbon aerogel decompose simultaneously such that they remain essentially in contact at their interfaces to form a monolithic glassy carbon material.

4. The method of Claim 1, wherein allowing said solution containing a plurality of carbon aerogel precurors to gel is carried out at a temperature of 80°C and a time period of 110 minutes.

8. The method of Claim 1, wherein pyrolyzing the dried composite is carried out in a furnace in the temperature range of 700 to 1100°C and for a time period of 8 to 12 hours.

18. The method of Claim 1, wherein said drying is carried out by supercritical carbon dioxide exchange.

IX. EVIDENCE APPENDIX

The attached Declaration was entered into the record by the Examiner as part of the applicants' response to the office action mailed July 20, 2004. The Declaration was mailed with a certificate of mailing on January 20, 2005 and was date stamped by the USPTO OIPE on January 25, 2005.

The attached paper (Lu et al., "Thermal and Electrical Conductivity of Monolithic Carbon Aerogels", 1993, pages 581-584, J. Appl. Phys. 73 (2) (1993)) was entered into the record by the Examiner as part of the applicants' response to the office action mailed July 20, 2004. The paper was mailed with a certificate of mailing on January 20, 2005 and was included in an Information Disclosure Statement date stamped by the USPTO OIPE on January 25, 2005.

The attached paper (Tajiri et al., "Effects of Supercritical Drying Media on Structure and Properties of Silica Aerogel", 1995, pages 83-87, J. Non-Cryst. Solids **186** (1995)) was entered into the record by the Examiner as part of the applicants' response to the office action mailed July 20, 2004. The paper was mailed with a certificate of mailing on January 20, 2005 and was included in an Information Disclosure Statement date stamped by the USPTO OIPE on January 25, 2005.

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Lawrence W. Hrubesh   Attorney Docket: IL-10413

Serial No. : 10/050,437   Art Unit: 1754

Filed : July 20, 2004   Examiner: P. Lish

For : Lightweight, High Strength Carbon
       Aerogel Composites And Method Of Fabrication

DECLARATION UNDER 37 CFR §1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

I, Lawrence W. Hrubesh, hereby declare that I am a citizen of the United

States of America and a resident of Pleasanton, California.

I have a PhD in Molecular Physics from the University of Wyoming.

I am a Physicist with the University of California, Lawrence Livermore

National Laboratory at Livermore, California.

I have worked at Lawrence Livermore National Laboratory as a Physicist

for 36 years. I have worked in the aerogel/sol-gel field at Lawrence Livermore

National Laboratory for 20 years.

I have read the office action and would like the examiner to consider my

comments in response to the rejections of claims 1, 4, 8 and 18.

Claims 1 and 18 are rejected as being anticipated by Droege. Claims 1, 4, 8

and 18 are rejected as being unpatentable over Pekala et al. in view of Kaschmitter. I

respectfully disagree with these rejections.

Table 1 of my application shows examples of the thermal conductivities of several types of carbon composites of aerogel loaded foam that were produced according to the method recited in claim 1. As confirmed in the attached reference: J. Appl. Phys. 73 (2) 1993, incorporated herein by reference, these thermal conductivities are very near to that of monolithic aerogels of comparable densities, which have average pore sizes that are less than 100 nm. This reference shows that low thermal conductivities in monolithic aerogels are the consequence of their unique morphology, consisting of particles and pores, which are smaller than the wavelengths of visible light. Moreover, this reference shows that such low conductivities would not be obtained if an aerogel was not truly monolithic (for example, if cracks, gaps, or large pores enabled paths for thermal energy to flow) and thus, if it did not have an average pore size less than 100 nm. It follows then that the monolithic glassy carbon composites of the present invention have average pore sizes that are less than 100 nm.

Monolithic aerogels are dried with special procedures, such as supercritical drying, that reduce surface tensile forces and minimize shrinkage, to produce these small pores. The present invention uses such drying procedures. It is well known in the art that using a supercritical drying step will produce an aerogel that has relatively small average pore size. See the attached reference: J. Non-Cryst. Solids 186 (1995), incorporated herein by reference. This reference shows that typical pore sizes for supercritically dried aerogels are less than 10 nm, even when different pore solvents are used (i.e., alcohols or carbon dioxide).

10

Claim 1 of my patent application includes a drying step that reduces surface tensile forces so that the organic aerogel and the preformed polymer foam/fiber-mat that it encapsulates, are essentially monolithic. After pyrolysis, they remain essentially in contact at their interfaces to form a monolithic glassy carbon material.

The Droege reference teaches a drying method that does not reduce surface tensile forces adequately to produce a monolithic composite, nor to form an essentially monolithic composite when pyrolized. The reference does not teach how to produce an essentially monolithic foam/mat aerogel composite. Therefore the rejection should be removed.
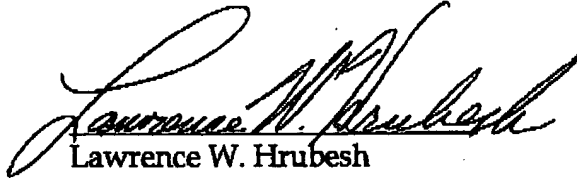
In both Pekala and Kaschmitter, the pore size is required to be large enough so that fluid (electrolyte) can flow. Thus, neither reference teaches a method for producing a monolithic foam/mat aerogel composite. The composites produced by the Pekala and Kashmitter patents do not exhibit the same bulk properties as a monolithic aerogel because the average pore size is relatively large. In fact, such large pores, which enable easy fluid transport through the material, are essential for the application of energy storage. Therefore the rejection should be removed.

Accordingly, I respectfully request that the rejections be withdrawn.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or

| |

both, under Section 1001 of Title 18 of the United States Code, and that such willful

false statements may jeopardize the validity of the application or any patent issued

thereon.

Respectfully submitted,

Dated: January 19, 2005   Lawrence W. Hrubesh

-4-

12

Thermal and electrical conductivity of monolithic carbon aerogels

Xianping Lu, Ove Nilsson, and Jochen Fricke

Physikalisches Institut der Universität, Am Hubland, D-8700 Würzburg, Germany

Richard W. Pekala

Chemistry and Materials Science Department, Lawrence Livermore National Laboratory, Livermore, California 94550

The thermal and electrical conductivity of monolithic carbon aerogels was investigated at room temperature. Results showed both the solid thermal conductivity and the electrical conductivity scale with the density in the range between 60 and 650 kg m^{-3}. The scaling exponents for the two conductivities have identical values of 1.5. For a density of 82 kg m^{-3} a thermal conductivity of 0.029 W m^{-1} K^{-1} in air and 0.018 W m^{-1} K^{-1} after evacuation was found.

I. INTRODUCTION

Aerogels are nanoporous materials produced in a sol-gel process followed by supercritical drying.[1-3] SiO$_2$ aerogels with densities of about 150 kg m^{-3} provide a low total thermal conductivity of 0.020 W m^{-1} K^{-1} at 300 K and in an atmosphere of 1 bar.[4] The tenuous solid skeleton leads to a very low solid thermal conductivity. The nanosized pores ($\Phi < 100$ nm) partially suppress the gaseous conduction in the pore space. The radiative conductivity in pure SiO$_2$ aerogels was found to be small at 300 K. However, it increases dramatically with temperature because the specific absorption coefficient of SiO$_2$ is extremely small for wavelengths below 8 μm.[4]

Recently, organic and opacified SiO$_2$ aerogels have become available, in which the infrared (IR) extinction is considerably higher than in pure SiO$_2$ aerogels.[5,6] Thus, the radiative transfer in such aerogels is significantly reduced. The smallest thermal conductivity values measured at ambient conditions for an organic aerogel and an opacified SiO$_2$ aerogel were 0.012 and 0.013 W m^{-1} K^{-1}, respectively.[5,6] Such aerogels have potential as substitutes for polyurethane foams blown with chlorofluorocarbons.

Dispersed carbon-based materials with graphitic nanostructure are efficient infrared absorbers, with a mass specific IR-extinction coefficient of more than 1000 m^2 kg^{-1}. Carbon-based fibers[7] and powders[8] are therefore effective high-temperature thermal insulations. Typically they have densities larger than 200 kg m^{-3} and provide thermal conductivities of about 0.1 W m^{-1} K^{-1} at room temperature and 0.3 W m^{-1} K^{-1} at 1000 °C. Due to the low density, monolithic carbon aerogels can be expected to have low thermal conductivities at high temperatures, too.

The scaling behavior of the thermal conductivity[9,10] and elastic modulus[11,12] with density have been derived experimentally for SiO$_2$ aerogels. The scaling is often discussed in terms of percolation theory. The measurements on various powders also showed that the percolation models are quite successful to describe the density dependence of the transport properties in such systems.[13,14] It would therefore be of interest to perform measurements of both the thermal and electrical conductivity on the carbon aerogels.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Carbon aerogels are derived from organic aerogels,[15,16] which are formed via the aqueous polycondensation of resorcinol with formaldehyde. In this polymerization process resorcinol serves as a trifunctional monomer capable of adding formaldehyde in the 2-, 4-, and 6-ring positions. Formaldehyde is bifunctional and forms covalent bridges between the resorcinol rings. The resultant sol is composed of polymer clusters, whose size is controlled by the concentration of the catalyst. The resorcinol–formaldehyde (RF) clusters cross-link to form a gel that is first exchanged with an organic solvent and then with liquid CO$_2$. The wet gel is transformed into a highly porous RF monolith via supercritical drying with respect to CO$_2$. The critical temperature for this gas is $T_c = 31$ °C and the critical pressure $p_c = 73.9$ bar. The RF aerogels are pyrolyzed in nitrogen at temperatures ranging from 600 to 1100 °C to form a carbon aerogel. All samples in this study were synthesized at a [resorcinol]/[catalyst] ratio of 200 and subsequently pyrolyzed at 1050 °C. For the thermal and electrical measurements the carbon aerogel samples are made in a block form with a size of 1.5×2×6 cm^3.

The thermal conductivity of carbon aerogels was measured at room temperature using a transient hot-wire technique.[17] A platinium hot wire is squeezed between a pair of identical aerogel blocks, as shown in Fig. 1. The thermal conductivity is determined by feeding a constant power into the wire and by observing its temperature increase with time.[17] In order to reduce thermal contact resistances between the wire and the aerogels, the surfaces of the samples were diamond turned. The elasticity of the aerogels allows proper embedding of the wire into the aerogel and helps to reduce the air slit between the blocks.

Instead of a bare wire a laquered Pt wire was used in order to avoid electrical contact of the Pt wire with the electrically conducting carbon aerogel specimens. The thickness d of the insulating layer was about 10 μm and the wire radius was 50 μm. The effects of the electrically insulating layer on the temperature increase of the wire have been analyzed by Nagasaka et al.[18] It was found that this effect is negligible for sufficiently long measuring times, i.e.,
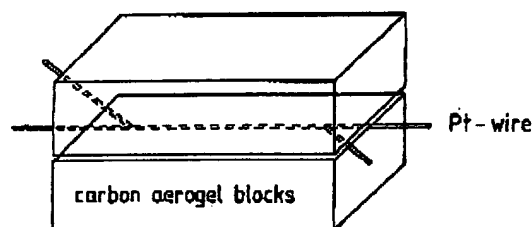
FIG. 1. Diagram of the aerogel sample with hot-wire probe for the measurements of the thermal conductivity.

if the penetration depth $\delta = \sqrt{\kappa t}$ of the thermal wave is much larger than the thickness d of the insulating layer. In our case the thermal diffusivities were $\kappa \gtrsim 3 \times 10^{-7}$ m^2 s^{-1} and measuring time larger than 10 s, $\delta/d \gtrsim 170$. Thus, the traditional long-time approximation[17] for the temperature increase can be used to determine the thermal conductivity.

Due to the small specimen sizes the length of the hot wire was limited to 50–60 mm. This may cause large axial heat losses through the potential leads. Calculations have shown that they can cause errors as large as 7% for the lowest thermal conductivities. The total relative uncertainty of the reported thermal conductivities is estimated to be less than 10%.

The thermal conductivity of various specimens was measured at room temperature as a function of gas pressure. The sample was mounted in a vacuum chamber, in which the gas pressure could be reduced to about 10^{-2} mbar.

The electrical conductivity at room temperature was measured using a four-probe technique (shown in Fig. 2). Electrical contacts were made by copper platelets, which guaranteed a reliable and intimate contact with the surface of the sample. The distance between the potential leads is about 5 cm. The main uncertainty in these measurements originates from the determinations of the distance between the voltage probes and the area of the specimen. The resulting errors in electrical conductivity are estimated to be less than 5%.

III. RESULTS AND DISCUSSION

The variation of the total thermal conductivity with gas pressure is depicted in Fig. 3. The lowest thermal conductivities at room temperature were obtained for a density of 82 kg m^{-3}: 0.029 W m^{-1}K^{-1} in air and 0.018 W m^{-1}K^{-1} when evacuated. The gaseous conductivities
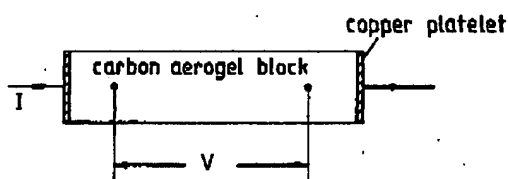

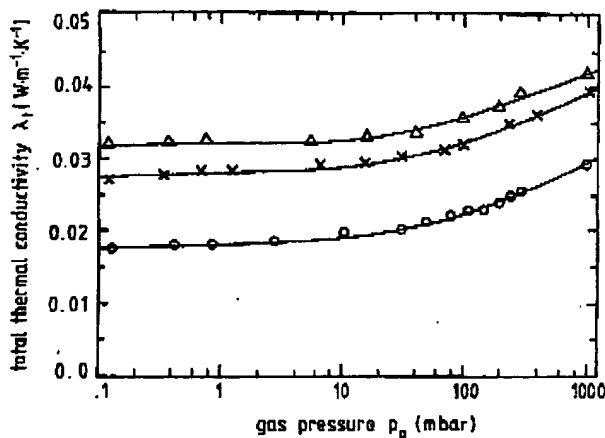FIG. 2. Diagram of the aerogel sample for the measurements of the electrical conductivity.

FIG. 3. Total thermal conductivity λ_t of various carbon aerogels vs air pressure p_g at room temperature; O : 82 kg m^{-3}; X : 124 kg m^{-3}, and Δ : 139 kg m^{-3}.

λ_g derived from the difference in thermal conductivity for the nonevacuated and the evacuated state, are in the range from 0.005 W m^{-1} K^{-1} (ρ=637 kg m^{-3}, not shown in Fig. 3) to 0.011 W m^{-1} K^{-1} (ρ=82 kg m^{-3}). As for organic and SiO$_2$ aerogels,[5,6] a systematic decrease of λ_g with increasing density is observed (see Fig. 4). A full suppression of gaseous thermal conduction occurs at a pressure of about 10 mbar.

The specific extinction coefficient was measured using a Fourier-transform infrared (FTIR) spectrometer[4] and found to be larger than 1000 m^2 kg^{-1}. Thus, the radiative contribution to the heat transfer at room temperature is negligible and the measurement of the thermal conductivity in the evacuated carbon aerogels directly provides the solid thermal conductivity.

Figure 4 shows the density dependence of the total thermal conductivity λ_t (nonevacuated specimen) and solid thermal conductivity λ_s (evacuated specimen) of car-
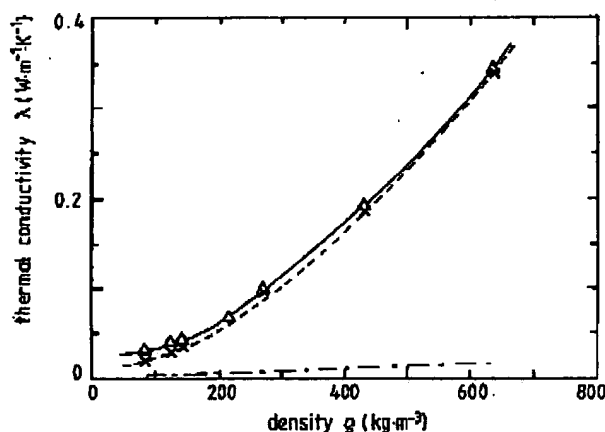

FIG. 4. Variation of the thermal conductivity λ with the density ρ for carbon aerogels in air (Δ) and under evacuation ($\times$). The line (–––––) depicts smoothed λ values calculated from the measured electrical conductivity using Eq. (1).

14

bon aerogels. A rapid increase of the thermal conductivity with density is observed.

It is of interest to know the relative contribution of the electrons to the thermal transport in carbon aerogels. Generally, the electronic thermal conductivity for metals and semimetals can be described by the Wiedemann–Franz law[19]

$$\lambda_e = \sigma TL, \qquad (1)$$

where T is the temperature and σ the electrical conductivity. The Lorenz number L can be expressed as[20]

$$L = L_0 - S^2. \qquad (2)$$

Where $L_0 = 2.45 \times 10^{-8}$ W Ω K^{-2} is the Lorenz number of free electrons and S the Seebeck coefficient. The value of L depends on the degree of degeneracy of the electron gas in the materials.

The Wiedemann–Franz law should also be applicable to carbon aerogels, which have a high carrier concentration of about 10^{20} cm^{-3}. Therefore, the electrical conductivity of carbon aerogels was measured as a function of density at room temperature. Values in the range from 0.6 to 20 Ω^{-1} cm^{-1} for densities between 60 and 650 kg m^{-3} were obtained. If we use the Lorenz number L_0 of free electrons and measured values of the electrical conductivity, we can estimate an upper limit for the electronic contribution to the thermal conductivity λ_e (see Fig. 4). The low values of λ_e indicate that the thermal conductivity of carbon aerogels is primarily due to the heat transfer by phonons.

Structural investigations[15] have shown that carbon aerogels form a chainlike network of small, highly disordered carbon spheres. The disordered nanostructure of carbon particles caused by the pyrolysis has been found to be similar to polycrystalline carbon.[15] An in-plane microcrystallite size of 2.5–3.0 nm was determined from Raman measurements. IR measurements and x ray studies support this conclusion for carbon aerogels.[21] It has been shown that the thermal transport even in nonporous polycrystalline graphite is mainly carried by phonons.[22] This was interpreted as the strong scattering from crystallite boundaries. The electronic heat transport in carbon aerogels seems also to be limited by scattering from the numerous boundaries.

The solid thermal conductivity of carbon aerogels is drastically reduced with respect to nonporous polycrystalline carbon. This is due to the large amount of pores existing in the medium, which restrict the propagation of local excitations to the chains in the tenuous skeleton.

Compared to organic[6] and SiO$_2$ aerogels,[5,23] carbon aerogels, however, provide a much lower thermal resistance. This is because nonporous carbon materials have much higher solid thermal conductivities than nonporous SiO$_2$ and organic materials under comparable conditions.[24] Furthermore, the elastic modulus for carbon aerogels obtained from ultrasonic measurements is significantly larger than their counterparts at the same porosity.[12] This indicates that a stronger bonding exists in carbon aerogels, which yield a better heat transfer between the particles.
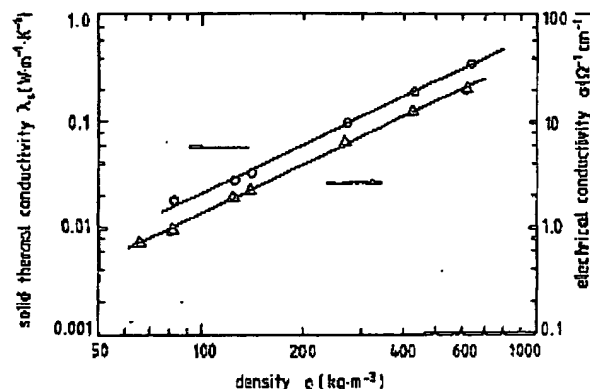

FIG. 3. The derived solid thermal conductivity λ_s (O) and electrical conductivity σ ($\triangle$) for carbon aerogels vs density ρ. The scaling exponents a and t, i.e., the slopes of the curves, are equal with $a = t = 1.5 \pm 0.1$.

Figure 5 shows that the thermal and electrical conductivity of carbon aerogels scale directly with the density of the skeleton

$$\lambda_s \propto \rho^a, \qquad \sigma \propto \rho^t. \qquad (3)$$

The best fits give identical values for the exponents $a = t = 1.5 \pm 0.1$, which is in good agreement with the results obtained for SiO$_2$ aerogels.[9,10]

A direct scaling behavior for the elastic modulus Y of the carbon aerogels has also been found.[12,25] The elastic exponent τ for the corresponding density range was determined to be 2.7 ± 0.2, which is smaller than the one for SiO$_2$ aerogels[12,26] ($\tau = 3.2$–3.8 in the density range above 100 kg m^{-3}).

The density dependence of the thermal and electrical conductivities can be described by the same scaling law with identical scaling exponents, although the thermal conductivity in the carbon aerogels is mainly due to phonon transport and not to electron transport. The same conclusion has been drawn for electrically conducting powders.[13] This indicates that the thermal and electrical conduction in these porous materials have identical conduction pathways. Furthermore, the results confirm that the scaling exponents for the two conductivities are significantly lower than the result for the elastic modulus. This is caused by the higher tensorial order of the elastic problem as compared to the electrical and thermal conduction process.[27] The ratio $\tau/a = \tau/t = 1.8$ coincides with the value 1.8 ± 0.2 determined for various powders.[13,14]

The scaling behavior of the transport properties is often discussed in terms of percolation theory. The measurements on the various powders[13,14] show that the thermal and electrical conductivity as well as the elastic modulus scale with $\rho - \rho_c$, where ρ_c is the percolation threshold. An interesting feature of monolithic aerogels is that the percolation threshold seems to be close to zero. This implies that a connective network exists for monolithic aerogels even at a very low density. The structure of aerogels can be characterized by percolation clusters,[28] but it is still controversial if critical phenomena for gelation are described cor-

15

rectly by percolation theory. The tenuous network of the gels may not be formed by randomly filling sites as in the percolation process.

ACKNOWLEDGMENTS

[1] J. Fricke, Ed., *Aerogels, Springer Proceedings in Physics 6* (Springer, Heidelberg, 1986).

[2] R. Vacher, J. Phalippou, J. Pelous, T. Woignier, Eds., *Proceedings of the 2nd International Symposium on Aerogels, Revue de Physique Appliquée 24* (Les Editions de Physique, Les Ulis Cedex, 1989), Vol. C4.

[3] J. Fricke, Ed., *Proceedings of the 3rd International Symposium on Aerogels*; J. Non-Cryst. Solids 145 (1992).

[4] R. Caps and J. Fricke, in *Aerogels, Springer Proceedings in Physics 6*, edited by J. Fricke (Springer, Heidelberg, 1986), p. 110.

[5] X. Lu, P. Wang, D. Büttner, U. Heinemann, O. Nilsson, J. Kuhn, and J. Fricke, "Thermal Transport in Opacified Monolithic Silica Aerogels," 12th European Conference on Thermophysical Properties, Vienna, Sept. 1990; High Temp.-High Pressures 23 (1991).

[6] X. Lu, M. C. Arduini-Schuster, J. Kuhn, O. Nilsson, J. Fricke, and R. W. Pekala, Science 255, 971 (1992).

[7] R. P. Tye, L. L. Lander, and K. Meiler, in *Thermal Conductivity 19*, edited by D. W. Yarbrough (Plenum, New York, 1988), p. 359.

[8] A. I. Lutkov, B. N. Lyukshin, and V. N. Mikhailov, Teplofiz. Vys. Temp. P6, 276 (1978).

[9] O. Nilsson, Å. Fransson, and O. Sandberg, *Aerogels, Springer Proceedings of Physics 6*, edited by J. Fricke (Springer, Heidelberg, 1986), p. 121.

[10] J. Fricke, X. Lu, P. Wang, D. Büttner, and U. Heinemann, Int. J. Heat Mass Transfer 35, 2305 (1992).

[11] T. Woignier, J. Pelous, J. Phalippou, R. Vacher, and E. Courtens, J. Non-Cryst. Solids 95-96, 1197 (1987).

[12] J. Gross, J. Fricke, R. W. Pekala, and L. W. Hrubesh, Phys. Rev. B 45, 12776 (1992).

[13] X. Lu, O. Nilsson, and J. Fricke, "Measurements of Thermal and Electrical Conductivity as well as Elastic Modulus of Electrically Conducting Powder Systems," 12th European Conference on Thermophysical Properties, Vienna, Sept. 1990; High Temp.-High Pressures 23, 149 (1991).

[14] O. Nilsson, X. Lu, and J. Fricke, *Thermal Conductivity 21*, edited by C. J. Cremers and H. A. Fine (Plenum, New York, 1990), p. 359.

[15] R. W. Pekala, J. Mater. Sci. 24, 3221 (1989).

[16] R. W. Pekala, C. T. Alviso, F. M. Kong, and S. S. Hulsey, J. Non-Cryst. Solids 145, 90 (1992).

[17] O. Nilsson, G. Rüschenpöhler, J. Gross, and J. Fricke, High Temp.-High Pressures 21, 267 (1989).

[18] Y. Nagasaka and A. Nagashima, J. Phys. E 14, 1435 (1981).

[19] P. G. Klemens, *Thermal Conductivity 1*, edited by R. P. Tye (Academic, London, 1969), p. 1.

[20] P. G. Klemens, *Thermal Conductivity 20*, edited by D. P. H. Hasselman and J. R. Thomas, Jr. (Plenum, New York, 1989), p. 63.

[21] J. Kuhn, Universität Würzburg, Germany (private communication).

[22] W. W. Tyler and A. C. Wilson, Phys. Rev. 89, 870 (1955).

[23] P. Scheuerpflug, H.-J. Morper, G. Neubert, and J. Fricke, J. Phys. D: Appl. Phys. 24, 1395 (1991).

[24] Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klemens, *Thermophysical Properties of Matter 2, Thermal Conductivity: Nonmetallic Solids* (Plenum, New York, 1970).

[25] R. W. Pekala, C. T. Alviso, and J. D. LeMay, J. Non-Cryst. Solids 125, 67 (1990).

[26] J. Gross and J. Fricke, J. Non-Cryst. Solids 145, 217 (1992).

[27] S. Feng, B. I. Halperin, and P. N. Sen, Phys. Rev. B 35, 197 (1987).

[28] D. W. Schaefer, Science 243, 1023 (1989).

Effects of supercritical drying media on structure and properties of silica aerogel

K. Tajiri [*], K. Igarashi, T. Nishio

National Industrial Research Institute of Nagoya, 1-1 Hirate-cho Kita-ku, Nagoya 462, Japan

Abstract

Silica alcogels prepared from tetramethylorthosilicate were supercritically dried with methanol, ethanol, 2-propanol and carbon dioxide media. The density, transmittance, specific surface area and pore size of the aerogels obtained were compared. The supercritical drying media affects the properties of the aerogel.

1. Introduction

Aerogels are porous materials prepared from wet gels (alcogels) by the supercritical drying method. Theoretically, the skeletal structure of wet gels is maintained through supercritical drying [1,2]. In aerogel preparation, however, slight shrinkage of the gel occurs. Alcohol [3,4] and carbon dioxide [5] are usually used as supercritical drying media. Hydrophobic aerogels are generally obtained using alcohol [6], and hydrophilic aerogels usually result from carbon dioxide extraction. This suggests that the type of medium affects the surface and structure of aerogels.

Silica aerogels were prepared from the same silica aerogels using different supercritical drying media (methanol, ethanol, 2-propanol and carbon dioxide) and the properties of the aerogels obtained were compared. The properties were observed 'to vary systematically with the media.

2. Experimental procedure

2.1. Preparation of aerogels

One mole of tetramethylorthosilicate (TMOS) was dissolved in 10 or 20 mol of methanol depending on the desired density. Six moles of water (containing NH_4OH of 0.1N concentration as catalyst) were added to the solution while stirring and the mixture was poured into molds. Silica alcogels were obtained by hydrolysis and gelation within 1–3 h. Disks with dimensions of 85 mm diameter and 10 mm thickness, and of 40 mm diameter and 10 mm thickness, and $10 \times 8 \times 80$ mm^3 bars were prepared in each alcogel lot. Alcogels were soaked in methanol, ethanol or 2-propanol for about 40 h to exchange the liquid phase of the gels for the medium used for supercritical drying. The samples prepared for CO_2 drying were exchanged to ethanol in this stage.

The autoclave used was 105 mm in diameter and 100 mm deep. An electric heater was wrapped around the side wall. Thermocouples were located near the electric heater (TC1) to control the heater temperature and at the center of the lid of the autoclave

[*] Corresponding author. Tel: +81-52 911 2111. Telefax: +81-52 916 2802. E-mail: tajiri@nirin.go.jp.

Table 1
Critical parameters for the supercritical drying media

Alcohol	Critical temperature (°C)	Critical pressure (MPa)
MeOH	239.4	8.09
EtOH	243.1	6.38
iPrOH	235.2	4.76
CO_2	31.1	7.38

(TC2). The temperature of TC2 was lower than the temperature of the inner samples and medium but the difference between them was less than 5°C.

Table 1 shows the critical parameters of the media used. Supercritical drying using alcohol as a medium was performed as follows. Alcogel samples were put into the autoclave and the autoclave was filled with alcohol and heated. The heating rate was 50°C/h to a temperature of 200°C and 25°C/h from 200°C to 300°C as measured by TC1. After reaching 300°C, the temperature was held constant until cooling was started. The pressure was kept at slightly above the critical pressure of the medium using a controlled leak. When the TC2 temperature reached 10°C above the critical temperature of the medium (usually about 1 h after TC1 reached 300°C), removal of the supercritical medium was started. The pressure was decreased to atmospheric pressure in 2 h, then the temperature was decreased to room temperature in 12 h.

For drying by carbon dioxide medium, the alcogel samples and ethanol were placed in the autoclave first. Then liquid carbon dioxide was fed into the autoclave for 2 h a rate of 20 ml/min at a temperature below 20°C to exchange ethanol with carbon dioxide. The pressure was kept above 7 MPa during this operation. This operation was repeated four times over 2 days, to complete the exchange. After that, the vessel was heated to 80°C (TC1) in 1 h, and when TC2 reached 40°C, removal of carbon dioxide was started.

Some aerogel samples were heat treated at 500°C for 2 h in air.

2.2. Measurements

The weight and dimensions of the samples were measured, and the bulk density and change of the volume, were calculated. Transmission spectra were

measured in the wavelength region 200–2500 nm by a UV/VIS spectrometer (Hitachi U-3400). The solar transmittance was calculated from the spectra. Specific surface areas and pore size distributions were measured by the Brunauer, Emmett and Teller (BET) nitrogen adsorption method (Carlo Erba Sorptomatic Model 1900). The skeletal density was measured by helium pycnometry (Shimazu-Micromeritics Autopycnometer Model 1320). The bending strength was measured by three-point bending test method with a Shimazu Autograph Model AG-25TC and 100g full scale load cell. Bar samples ($10 \times 8 \times 80$ mm^3, but actual dimensions were smaller because of shrinkage) were used for the bending strength measurements.

3. Results

Two types of silica alcogel, MeOH/TMOS mole ratio of 10 (shown by the notation H in the figures) and 20 (shown by L), were used for the experiments. The bulk density of the aerogels as removed from autoclave (shown by the notation before H.T. in the figure) and those measured after heat treatment (shown by after H.T.) are shown in Fig. 1. The density varied considerably with the kind of the supercritical drying media and the heat treatment used. Fig. 2 shows the volume and weight change from the heat treatment process. Shrinkage occurred during both supercritical drying and heat treatment. In both processes, aerogels dried by 2-propanol showed the largest shrinkage. Next were those dried
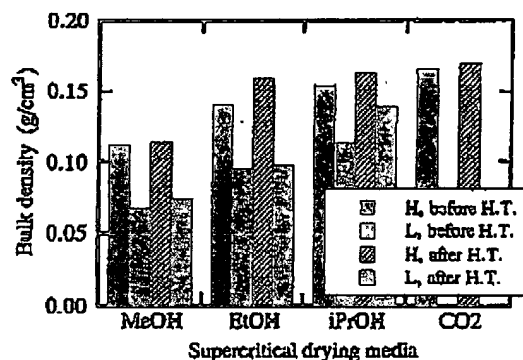

Fig. 1. Density of silica aerogels: H denotes alcogel was prepared as [MeOH/TMOS] = 10; L denotes [MeOH/TMOS] = 20; H.T. denotes heat treatment.
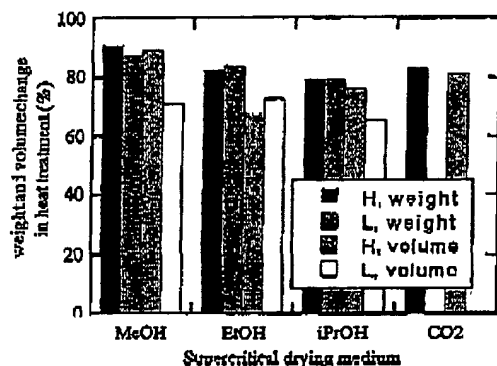
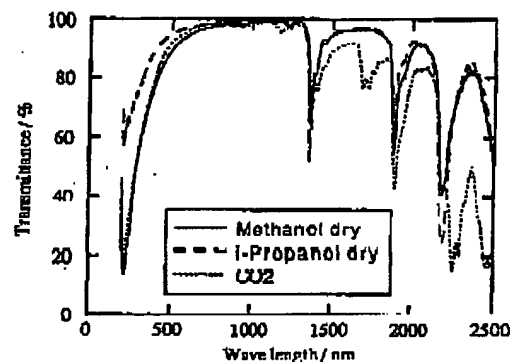Fig. 2. Weight and volume change of aerogels by heat treatment.

Fig. 4. Transmission spectra of aerogels after heat treatment.

by ethanol, and those dried by methanol showed the smallest shrinkage. There was less shrinkage for the higher-density aerogels. Weight loss also occurred during the heat treatment process. The order of the weight loss was 2-propanol > ethanol > methanol. However the silica concentration (— bulk density of aerogel) had no effect to the percentage loss.

Fig. 3 shows transmission spectra of samples before heat treatment. The difference in the position of small absorption bands indicates the difference of the materials remaining on the surface of the aerogels. The spectra of samples after heat treatment are shown in Fig 4. The position of the principal absorption bands was almost the same as that of the samples dried by carbon dioxide. This means that hydroxyl groups existed on the surfaces.

Fig 5 shows the solar transmittance and specific surface areas. The solar transmittance was improved by the heat treatment. In particular, aerogels dried by 2-propanol have about 96% transmittance for 10 mm thickness, and they show a significant improvement

over other aerogels for transmittance below 500 nm wavelength, as shown in Fig. 4. Specific surface areas become larger with the heat treatment. Pore size distributions for samples before heat treatment dried by methanol and by 2-propanol are shown in Fig. 6. The pore size of methanol dried aerogel was about 60–70 Å, and that of 2-propanol-dried aerogel was about 40 50 Å.

Fig. 7 shows the skeletal densities. The skeletal densities of aerogels after heat treatment were 2.02–2.09g/cm³, and slightly less than 2.2g/cm³ for amorphous silica. The skeletal densities before heat treatment decreased systematically for methanol-dried to 2-propanol-dried.

The bending strength is shown in Fig 8. The strength increased with bulk density as previously reported [7]. However, our data varied widely, so that no statistically significant effect of drying media was found.
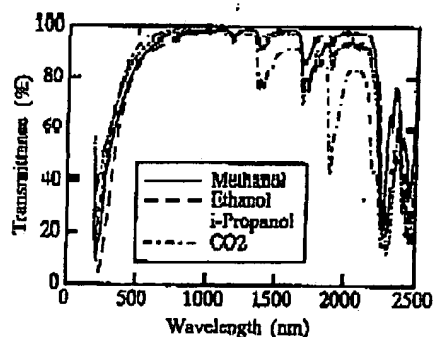

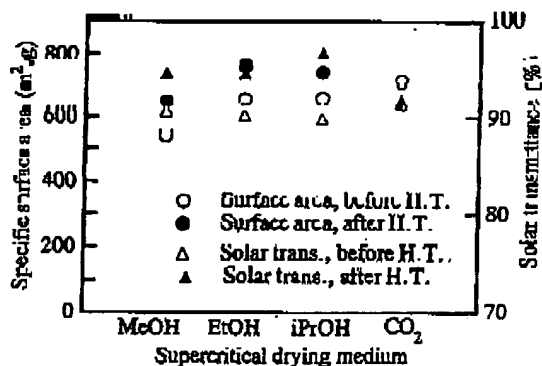Fig. 3. Transmission spectra of aerogels before heat treatment.

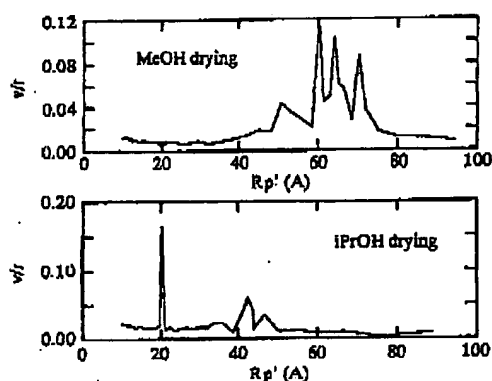Fig. 5. Specific surface area and solar transmittance of aerogels.

Fig. 6. Pore size distribution of methanol-dried and 2-propanol-dried aerogels.
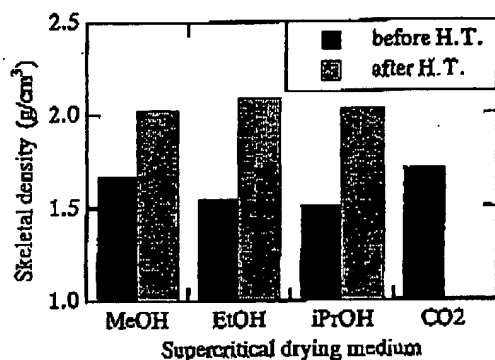

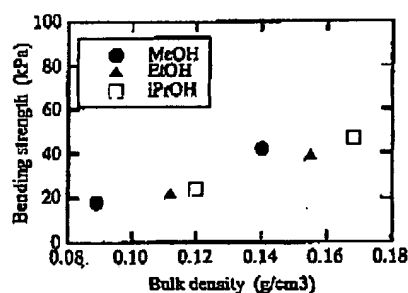Fig. 7. Skeletal density of aerogels before and after heat treatment.

Fig. 8. Bending strength of aerogels before heat treatment.

4. Discussion

With supercritical drying using alcohol, the surface of the aerogel is covered by corresponding alkyl groups. The aerogels obtained are hydrophobic, and transmission spectra support this observation. Surface alkyl groups are removed by oxidation and the skeletal density is increased by heat treatment [8,9]. The weight loss from the heat treatment indicates

that the ratio of alkyl groups to silica changes. If alkyl groups are removed from aerogels dried by methanol, ethanol and 2-propanol, respectively, the molar ratio of alkyl group to silica is consistent (0.47) for all aerogels within 10% error. This suggests that alkyl groups exist on silica surface with the same concentration, and the size of alkyl group affects the aerogel properties. If the same number of alkyl groups exists on the same silica skeletal network the alkyl group with larger volume makes the pore size of the network smaller, and larger alkyl group makes the skeletal density of the aerogel smaller because the molar density of alkyl groups is smaller than that of silica. The experimental results that the pore size of the aerogel dried by 2-propanol was smaller than that of the aerogel dried by methanol, and that the skeletal density became systematically smaller with the size of alkyl group, agree with this suggestion. Small-angle X-ray scattering and Raman scattering data also show that the particle sizes become larger with the size of the alkyl group [10]. These changes of structure do not affect the aerogel strength within our detection limits.

If the skeletal structure of an aerogel which was constructed during gel formation was not affected by the drying process, then aerogels which underwent heat treatment should have the same properties. However, the transmittance and bulk density of the aerogels varied with supercritical drying media. For example, significant improvement of the transmittance of heat-treated 2-propanol-dried aerogel is considered to be caused by the smaller skeletal particle size. This suggests that skeletal particles of the aerogel dried by 2-propanol shrink more in sintering than those of aerogels dried by other media, but it does not explain why the type of the supercritical drying medium affects the shrinkage of the skeletal particle size in sintering. We conclude that the supercritical drying medium affects the aerogel structure, but further study is needed to understand this effect.

5. Conclusion

Supercritical drying media affect the properties of aerogels obtained. The surface of the aerogels prepared by supercritical drying of alcohol is covered by the corresponding alkyl groups, and the size of

the alkyl group affects the aerogel properties, such as pore size. The aerogel prepared by supercritical drying of 2-propanol and heat treated shows excellent transparency.

References

[1] S.S. Kistler, Nature 127 (1931) 741.

[2] J. Fricke, J. Sci. Am. 1988 (1988) 92.

[3] G.A. Nicolaon and S.J. Teichner, Bull. Soc. Chim. France 1968 (1968) 1906.

[4] S. Henning, in: Aerogel (Proc. 1st Int. Symp. on Aerogels, ISA1) (Springer, Berlin, 1986) p. 38.

[5] P.H. Tewari, A.J. Hunt and K.D. Lofftus, Mater. Lett. 3 (1985) 363.

[6] S.J. Teichner, G.A. Nicolaon, M.A. Vicarini and G.E.E. Gardes, Adv. Colloid Interf. Sci. 5 (1976) 245.

[7] T. Woignier and J. Phalippou, J. Non-Cryst. Solids 100 (1988) 404.

[8] J. Zarzycki and T. Woignier, in: Aerogel (Proc. 1st Int. Symp. on Aerogels, ISA1) (Springer, Berlin, 1986) p. 42.

[9] J. Phalippou, T. Woignier and M. Prassas, Rev. Phys. Appl. 24 (C4)(1989) 47.

[10] K. Igarashi, K. Tajiri, T. Asahina and S. Tanemura, in: Proc. ISES Congr., Budapest, 1993, Harmony with Nature, Vol. 2, ed. A. Zold (Hungarian Solar Energy Society, Budapest, 1994) p. 469.

X. <u>RELATED PROCEEDINGS APPENDIX</u>

None